

LWL  
TR-74-83  
c. 1

TECHNICAL REPORT NO. 74-83

IMPROVED FIELD WATER ANALYSIS TESTS

by

Harold Rosen  
Biological Sciences Branch

TECHNICAL LIBRARY  
BLDG. 305  
ABERDEEN PROVING GROUND, MD.  
STEAP-TL

May 1974

Final Report

COUNTED IN

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

U. S. ARMY LAND WARFARE LABORATORY  
Aberdeen Proving Ground, Maryland 21005

LWL  
TR-74-83  
c. 1

20081009209

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products.

## UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER  TECHNICAL REPORT NO. 74-83	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle)  Improved Field Water Analysis Tests		5. TYPE OF REPORT & PERIOD COVERED  Final Report
7. AUTHOR(s)  Harold Rosen Biological Sciences Branch		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS  US Army Land Warfare Laboratory Aberdeen Proving Ground, MD 21005		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS  LWL Task No. 01-B-74
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE  May 1974
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES  10
		15. SECURITY CLASS. (of this report)  Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Water testing Chloride test for water Alkalinity test for water Sulfate test for water Water analysis		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Three tests which had previously been developed under LWL Task 03-B-69 for a candidate kit reported on in Technical Report No. LWL-CR-03B69 were sent to TECOM for testing. These tests were for chloride, alkalinity and hardness. The chloride and alkalinity partially met the criteria, the hardness test failed to meet the criteria. In addition a new test for sulfate was developed which shows much promise but which must be tested and developed further.		

AD-782104

PREFACE

Appreciation is expressed to Mr. Hugh Morison of the Ames Company for providing materials for testing; to Messrs. Peter Kamenik and David Phillips of the US Army Test and Evaluation Command for their cooperation in the testing phase; and to Dr. Peter Mitchell and Ms. Tamar Der Ohanessian of Franklin Institute Research Laboratories for an outstanding job in the sulfate test development.

## ABSTRACT

Under Work Assignment No. 3 of Contract DAAD05-74-C-0723 by the Franklin Institute Research Laboratories (FIRL) for the U.S. Army Land Warfare Laboratory, an improved test for Sulfate in Water was developed based on the LWL-recommended reagent barium chloranilate. The paper test strips operate in the range of from 100-3000 mg/l of sulfate ion. Their sensitivity in the lower sulfate levels is sufficient to differentiate 50 mg/liter from 100 mg/liter.

## FOREWORD

This report is submitted in compliance with contractual requirements as directed by the U.S. Army Land Warfare Laboratory, Aberdeen Proving Ground, Maryland, under Contract No. DAAD05-74-C-0723. Mr. Harold H. Rosen, Biological Sciences Branch, served as Technical Supervisor for the work, and we would like to acknowledge his recommendation of the barium chloranilate reagent which made the development of the test strips possible.

## CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
	ABSTRACT . . . . .	i
	FOREWORD . . . . .	ii
1.	INTRODUCTION . . . . .	1-1
2.	CONCLUSIONS . . . . .	2-1
3.	THEORETICAL . . . . .	3-1
4.	EXPERIMENTAL . . . . .	4-1
	4.1 Preparation of Barium Chloranilate . . . . .	4-1
	4.2 Experiments with Filter Paper Strips . . . . .	4-1
	4.3 Experiments with Papers Impregnated with Barium Chloranilate . . . . .	4-2
	4.4 Methods for Coating the Papers . . . . .	4-2
	4.5 Procedure . . . . .	4-3
	4.6 Calibration . . . . .	4-4
5.	REFERENCES . . . . .	5-1
	APPENDIX . . . . .	A-1

## FIGURES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1.	Calibration Curve . . . . .	4-5
2.	Photograph of Test Strips . . . . .	4-6

## INTRODUCTION

An effort to update water quality test procedures for field use was undertaken at LWL as a result of a study by ACTIV of Army water supply operations in the Republic of Vietnam.<sup>1</sup> The ACTIV report discussed the shortcomings of the water test kit then available for field use, which dated back to WWII, and recommended that the kit be updated. Somewhat after the initiation of the LWL task, a proposed Small Development Requirement covering the development of Engineer, Preventive Medicine and Medical Laboratory water quality test kits was issued and formalized. This SDR was later converted to a Materiel Need document, and the Mobility Equipment Research and Development Center (MERDC) at Fort Belvoir was assigned development responsibility. The LWL effort was coordinated with MERDC.

It was recognized at the outset of the LWL effort that a water test kit for field use should be as simple, compact, rugged and easy to use as would be compatible with realistic criteria of accuracy and precision. Not only the obsolete WWII kit that was originally supplied to field units in Vietnam, but even a modern commercial kit that subsequently was procured by the Army on an interim basis for use in Vietnam, were bulky and required skilled manipulation of reagents and fragile glass components. A survey of the current state-of-the-art revealed that simple "dip-strips," that need only be dipped into water to make a test, were available commercially for a number of the water constituents of interest. For example, so-called Quantabs were on the market to test for chloride, alkalinity, acidity, and later, for total hardness.<sup>2</sup> These test strips were incorporated in the LWL prototype kit shown in Figure 1.<sup>3</sup> Other components of comparable simplicity and ease of operation that comprised the LWL kit included tests for sulfate, residual chlorine, pH, turbidity, flocculation and chlorine demand. A typical test strip from the kit is shown in Figure 2. In operation the strip is dipped into a water sample for a given length of time which causes a color change. The height of the color change is read on the scale and converted to parts per million using a chart provided. Another one of the strip tests relies on comparison of a color change with a color chart.

Several LWL prototype kits were furnished to MERDC for evaluation. Components of the kit were subsequently tested by the Army Environmental Hygiene Agency, which had been tasked by MERDC to obtain and test all commercially available tests and to select components for a standardized Army kit. In its tests, AEHA found that the LWL kit components were by far the simplest to use but were not the best in terms of accuracy and precision.<sup>4</sup> Because of the demonstrable simplicity and ease of use of the LWL test strips, AEHA did

---

<sup>1</sup>Water Supply in the Republic of Vietnam. Final report, ACTIV Project ACL-22F, Dec 67.

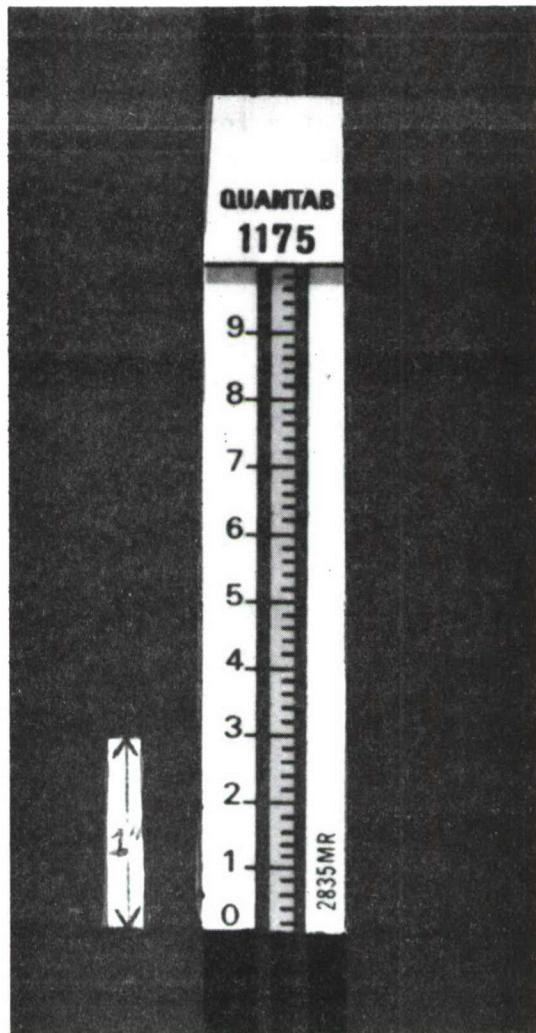
<sup>2</sup>Manufactured by the Ames Co., Elkhart, IN.

<sup>3</sup>Improved Water Analysis Kit, LWL Technical Report No. LWL-CR-03B69, Dec 72.

<sup>4</sup>Water Quality Engineering Special Study R&D No. 24-001-71-72, US Army Environmental Hygiene Agency, 1 Nov 72.



Figure 1. Water Analysis Kit



**Figure 2.** Typical Dip Strip from the LWL Water Analysis Kit

recommend that the LWL tests be further developed. On the basis of this recommendation, LWL instituted the program described in the present report (LWL Task 01B74). This program included additional testing of the commercial chloride, alkalinity and hardness dip tests and further development of the sulfate test. The original sulfate test vehicle was a reagent spot on a glass slide, and the purpose of further development was to see if an impregnated paper strip could be substituted for the glass slide, making this test comparable to the other dip tests.

## EVALUATION OF SELECTED DIP TESTS

The USA Test and Evaluation Command (TECOM) was requested to perform a product improvement test of the chloride, alkalinity and hardness dip tests in conjunction with a Development Test (DT) (Engineering Phase) II of water quality analysis sets being performed for MERDC. The criteria established for the MERDC development test were employed in the product improvement test to ascertain how closely the LWL components met Army requirements.

The criteria against which the test strip were evaluated, the evaluation procedures and the test results are described in detail in a TECOM report included here as Appendix A.<sup>5</sup> Briefly summarized, the TECOM test results showed that the chloride and alkalinity test strips partially met the criteria and the hardness test strips did not meet the criteria.

## DEVELOPMENT OF SULFATE TEST

A prototype paper dip strip to test for sulfate in water was developed by the Franklin Institute Research Laboratories of Philadelphia under a contract with LWL (see Appendix B). Although the development effort was successful in demonstrating feasibility, with the phasing out of LWL it was not possible to undertake a program of test and further refinement to establish whether the sulfate dip strip can meet the Army criteria.

---

<sup>5</sup>Final Letter Report of Product Improvement Test of Improved Field Water Analysis Tests, LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003, Report No. APG-MT-4417, Feb 74.

## DISCUSSION

The TECOM results showed that the chloride and alkalinity test strips met the criteria for accuracy except near the lower range limits of concentration. It is considered that only a relatively simple manufacturing adjustment would be required to produce chloride and alkalinity test strips that would fully meet the criteria. Complete failure of the hardness strips, on the other hand, as shown by the TECOM results, indicates that the test strip reagent-matrix composition does not have the necessary sensitivity to provide adequate resolution within the required range; additionally the present composition may be not sufficiently stable to give acceptably reproducible values. Whether these deficiencies can be corrected merely by improved quality control during manufacture or whether further development and testing are required to produce an acceptable hardness test strip cannot be determined without a careful study of the present test strip composition and reaction characteristics.

## CONCLUSIONS

1. The chloride and alkalinity test strips partially met the criteria.
2. The hardness test strips failed to meet the criteria.
3. A dip strip test for sulfate is feasible.

## RECOMMENDATIONS

It is recommended that:

1. TROSCOM procure and retest chloride and alkalinity test strips modified to meet the specified criteria.
2. TROSCOM initiate development to perfect dip strip tests for hardness and sulfate, and other tests in the Water Quality Analysis Set, Engineer.
3. The Office of the Surgeon General pursue development to apply the dip strip test concept to the Water Quality Analysis Set, Preventive Medicine.

APPENDIX A

FINAL LETTER REPORT OF  
PRODUCT IMPROVEMENT TEST OF IMPROVED FIELD WATER ANALYSIS TESTS



DEPARTMENT OF THE ARMY  
ABERDEEN PROVING GROUND Mr. Kamenik/sjw/870-2510  
ABERDEEN PROVING GROUND, MARYLAND 21005

STEAP-MT-F

28 FEB 1974

SUBJECT: Final Letter Report of Product Improvement Test of Improved Field Water Analysis Tests, LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003, Report No. APG-MT-4417

Commander  
US Army Land Warfare Laboratory  
ATTN: AMXLW-TS

1. REFERENCES:

- a. Letter, AMXLW-TS, 14 Sep 73, subject: Improved Field Water Analysis Tests, LWL Task 01-B-74, AMCMS No. 673701.12.71900.
- b. Letter, AMSTE-GE, 4 Oct 73, subject: Test Directive, Product Improvement Test of Improved Field Water Analysis Tests, LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003.
- c. Letter, CDCMS-0, 7 Aug 72, subject: Department of the Army Approved Materiel Need (Engineering Development) (MN(ED)) for Water Quality Analysis Set, Engineer.
- d. Test Plan, Development Test (DT) (Engineering Phase) II of Water Quality Analysis Sets, Engineer, Preventive Medicine and Medical Laboratory, TECOM Project No. 7-ES-225-000-001, Sep 73.

2. BACKGROUND:

- a. The US Army Land Warfare Laboratory (LWL) has developed a water analysis kit for use in lieu of the current standard Water Quality Control Set, FSN 6630-262-7288. In a letter (reference a) to the US Army Test and Evaluation Command (TECOM), LWL requested that components (Improved Field Water Analysis Tests) of this kit be evaluated in conjunction with the Water Quality Analysis Sets described in reference d. A test plan outline, attached as Inclosure 1, was prepared to confirm the exact methods and procedures which would be utilized to evaluate the test items.

STEAP-MT-F

SUBJECT: Final Letter Report of Product Improvement Test of Improved Field Water Analysis Tests, LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003, Report No. APG-MT-4417

b. The test items to be evaluated are those for determining chlorides, alkalinity, and hardness. The chloride and alkalinity tests consist of 3-inch long by 1/2-inch wide capillary strips which have a graduated backing card that is interpreted by reference to a calibration table. The strips are treated to detect chlorides or alkalinity respectively. The hardness test is a chemically treated spot and color comparison chart for determining the reading. The test items eliminate the necessity to manipulate fragile glassware or to prepare or measure reagents.

c. The purpose of the test was to determine how the improved field water tests compare with the requirements specified in reference c. Two hundred and fifty chloride test strips and three hundred each of the alkalinity and hardness test strips were provided for testing. A number of each were exposed to solutions of known concentration to verify their range and accuracy. This evaluation was conducted at Aberdeen Proving Ground (APG) during the period from 26 November 1973 through 11 February 1974.

### 3. TEST OBJECTIVES:

a. To determine the range, accuracy, and precision of the test items.

b. To determine the degree to which the test items meet the performance requirements for chlorides, alkalinity, and hardness of the approved Materiel Need (MN).

### 4. SUMMARY OF RESULTS:

a. The test plan outline, attached as Inclosure 1, provides details of the procedure used in evaluating the improved field water tests. Also, attached as Inclosure 2 are the appropriate excerpts from reference d which are referenced in the test plan outline.

b. Standard solutions were made up for each required concentration and for the end points on the range specified by the manufacturer and the test was conducted as follows:

1) Chloride Test - Standard solutions were prepared with sodium chloride to concentrations of 36, 250, 600, 1000, and 1200 parts per million (ppm) chloride ( $Cl^-$ ). The chloride test strip was placed

STEAP-MT-F

SUBJECT: Final Letter Report of Product Improvement Test of Improved Field Water Analysis Tests, LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003, Report No. APG-MT-4417

vertically in a beaker containing one of the aforementioned chloride concentrations. The liquid level in the beaker was enough to emerse only half the strip. The strip was left in the beaker until the self-timing indicator (a spot at the top which turns blue when water reaches it - approximately 12 minutes) turned blue. Each strip was read and the result recorded. The results of up to 57 repeated tests are provided in Table 4-1, Inclosure 3.

2) Alkalinity Test - The criteria in the MN(ED) (reference c) is based on calcium carbonate ( $\text{CaCO}_3$ ) as a measure of alkalinity. The improved field water analysis alkalinity test is based on sodium hydroxide ( $\text{NaOH}$ ). Consequently, to comparatively evaluate the test, a calibration curve was prepared using, as a reference, standard solutions of sodium carbonate. Solutions equivalent to 7500, 500, 125, and 120 mg  $\text{CaCO}_3/1$  were prepared.

The alkalinity test strip was placed vertically in a beaker containing one of the aforementioned solutions at a level so as to emerse only half the strip. The strip was left in the beaker for approximately 15 minutes. The strip was removed, allowed to develop approximately 30 seconds, read, and the result recorded. Table 4-2, Inclosure 3, provides the results of up to 53 repeated tests.

3) Hardness Test - Standard solutions of calcium chloride were prepared to provide the equivalent in hardness to 0, 20, 250, and 425 ppm as calcium carbonate ( $\text{CaCO}_3$ ). A test strip was dipped in one of the solutions and removed immediately. Excess solution was shaken from the strip. The color which developed after about 15 seconds was compared with the color chart provided on the jar of test strips. The results of up to 61 repeated tests are provided in Table 4-3, Inclosure 3.

c. For each standard solution, the average concentration, the standard deviation about the average and the 95% confidence interval on the mean concentration were calculated. The 95% tolerance interval, for which it may be said with 95% confidence at least 90% of the concentration population lies, was also calculated. The results of these determinations are provided in Tables 4-4, 4-5, and 4-6, Inclosure 3. Plots relating deviation and known concentration, where deviation is the average observed concentration minus the known concentration, are given in Figures I, II, and III, Inclosure 4.

STEAP-MT-F

SUBJECT: Final Letter Report of Product Improvement Test of Improved Field Water Analysis Tests, LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003, Report No. APG-MT-4417

5. CONCLUSIONS:

a. The chloride test strips partially meet the criteria. The requirement for range of 10 to 1200 ppm is not met since the chloride test strip with a range of 36 to 1200 ppm cannot detect to the lower limit required. The accuracy requirement is considered to have been met. The 95% Confidence Interval on the Mean (CIM) is within the criteria accuracy interval for the 600 ppm  $\text{Cl}^-$ . The 95% CIM upper limit exceeds the upper limit of the accuracy interval for 250 and 1000 ppm  $\text{Cl}^-$ . The 95% Tolerance Interval (90% of concentration population with 95% stated confidence) indicate values within the lower limit requirements for 250, 600, and 1000 ppm  $\text{Cl}^-$ , however, all three upper limit requirements were exceeded.

b. The alkalinity test strips partially meet the criteria. The range requirement is not met since the strips cannot detect the lower range limit of 5 mg/l as  $\text{CaCO}_3$ . The strip range, as stated by the manufacturer, is 0.01 to 0.6%  $\text{NaOH}$  which equates to a range of 125 to 7500 mg/l as  $\text{CaCO}_3$ . The required range is 5 to 500 mg/l as  $\text{CaCO}_3$ . The accuracy requirement is considered to have been met since the 95% Confidence Interval on the Mean falls within the accuracy interval for the most part (see Table 4-5, Inclosure 3). The deviation from the known concentration however increases greatly (332.8 ppm versus 6.8 to 13 ppm) at the high range.

c. The hardness test strips do not meet the criteria. The required range is 20 to 9000 mg/l as  $\text{CaCO}_3$ . The manufacturer stated strip range is only 0 to 425 mg/l as  $\text{CaCO}_3$  (0 to 425 ppm  $\text{CaCO}_3$ ). In addition, the results obtained for the 250 and 425 mg/l solutions were almost the same (see Table 4-3, Inclosure 3). This indicates the upper limit of the upper limit at 110 to 140 mg/l as  $\text{CaCO}_3$ . The hardness test strips did not meet the accuracy requirement of  $250 \pm 33$  mg/l as  $\text{CaCO}_3$ . The 95% CIM has an upper limit of 117.2 mg/l and a lower limit of 104.8 mg/l as  $\text{CaCO}_3$ . Also the 95% Tolerance Interval indicates that 90% of the concentration population lies between 64.3 and 157.7 mg/l as  $\text{CaCO}_3$ . The

STEAP-MT-F

SUBJECT: Final Letter Report of Product Improvement Test of Improved  
Field Water Analysis Tests, LWL Task 01-B-74, TECOM Project  
No. 7-ES-225-000-003, Report No. APC-MT-4417

average concentration is in error by 55.6%. A review of the method used revealed nothing that would explain these results. It was therefore concluded that the results indicate a failure of the hardness test strips rather than the method used.

FOR THE COMMANDER:

4 Incl  
as



H. A. BECHTOL  
Acting Associate Director  
Materiel Testing Directorate



DEPARTMENT OF THE ARMY  
ABERDEEN PROVING GROUND Mr. Kamenik/sjw/870-2510  
ABERDEEN PROVING GROUND, MARYLAND 21005

STEAP-MT-F

8 6 NOV 1973

SUBJECT: Test Plan Outline for Testing Improved Field Water Tests,  
LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003

Commander  
US Army Land Warfare Laboratory  
ATTN: AMXLW-TS

1. REFERENCES:

- a. Letter, AMSTE-GE, 4 Oct 73, subject: Test Directive, Product Improvement Test of Improved Field Water Analysis Tests, LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003 (Inclosure 1).
- b. Test Plan, Development Test (DT) (Engineering Phase) II of Water Quality Analysis Sets, Engineer, Preventive Medicine and Medical Laboratory, TECOM Project No. 7-ES-225-000-001, Sep 73 (Inclosure 2).
- c. Letter, CDCMS-0, 7 Aug 72, subject: Department of the Army Approved Materiel Need (Engineering Development) (MN(ED)) for Water Quality Analysis Set, Engineer.

2. BACKGROUND:

The US Army Land Warfare Laboratory (LWL) has developed a water analysis kit for use in lieu of the current standard Water Quality Control Set, FSN 6630-262-7288. In a letter (reference a) to the US Army Test and Evaluation Command (TECOM), LWL requested that components (Improved Field Water Analysis Tests) of this kit be evaluated in conjunction with the Water Quality Analysis Sets described in reference b. This test plan outline was prepared to confirm the exact methods and procedures which will be utilized to evaluate the test items.

3. DESCRIPTION OF MATERIEL:

The test items to be evaluated are chlorides, alkalinity, and hardness tests. The chloride and alkalinity tests consists of 3-inch long by 1/2-inch wide capillary strips which have a graduated backing card that is interpreted by reference to a calibration table. The strips are treated to detect chlorides or alkalinity respectively. The

STEAP-MT-F

26 NOV 1973

SUBJECT: Test Plan Outline for Testing Improved Field Water Tests,  
LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003

hardness test is a chemically treated spot and color comparison chart for determining the reading. The test items eliminate the necessity to manipulate fragile glassware or to prepare or measure reagents.

4. TEST OBJECTIVES:

- a. To determine the range, accuracy, and precision of the test items.
- b. To determine the degree to which the test items meet the performance requirements for chlorides, alkalinity, and hardness of the approved Materiel Need (MN).

5. TEST PROCEDURE:

The test items will be evaluated in accordance with paragraphs 2.3.2a4), 6), and 8); 2.3.3 (with the exception of interference evaluations); and 2.3.4.1d, f, and h of reference b. The analytical plan will be as follows:

For each sample of measurements for the 3 test items, the average concentration, the standard deviation about the average, and the 95% confidence interval on the mean concentration will be calculated. The accuracy criteria will be considered to have been met if the confidence interval on the mean concentration falls within the criteria interval. The range criteria will be considered to have been met if the kit can provide results over the criteria decision concentration range.

For each sample, the 95% tolerance interval will also be calculated. This will be the interval in which it may be stated with 95% confidence at least 90% of the concentration population lies.

It is assumed that concentration measurements are normally distributed random variables.

Curves will be plotted relating deviation and known concentration where the deviation is the average observed concentration minus the known concentration.

STICAP-MT-F

26 NOV 1973

SUBJECT: Test Plan Outline for Testing Improved Field Water Tests,  
LWL Task 01-B-74, TECOM Project No. 7-ES-225-000-003

6. GENERAL INFORMATION:

The cost estimate submitted to TECOM was based on the above plan of test. Any increase in the scope of test from that presented will require additional funds.

FOR THE COMMANDER:

2 Incl  
as

H. A. BECHTOL  
Acting Associate Director  
Materiel Testing Directorate

CC:  
Cdr, TECOM  
ATTN: AMSTE-GE

## 2.3 CHEMISTRY PERFORMANCE

### 2.3.1 Objectives

- a. To determine the degree to which the water quality analysis sets (ES, PMS, and MLS) are capable of detecting the chemical elements and compounds as specified in the MN(ED) documents for each of the three sets.
- b. To determine if the measurement accuracies of the ES, PMS, and MLS are as specified in the Purchase Description for Water Quality Analysis Sets, 4 October 1972 and the DASG Recommended Performance Criteria (Reference 5).

### 2.3.2 Criteria (Criteria utilized in bracketed)

- a. The Water Quality Analysis Set, Engineer, shall provide equipment, chemicals and accessories to permit the operator to perform the following tests (MN(ED), ES, Section VI, para b(5)).
  - 1) Turbidity. The turbidity measurements for determining filter performance will be within the range of 5 to 10 units and for selection of raw water sources will be within the range of 25.0 to 200 units. High turbidities require greater expenditure of operating chemical supplies for water treatment (MN(ED), ES, Section VI, para b(5)(a); CTP, Revision 1, Table III). The accuracy of the kit shall be as follows: 5 JTU  $\pm$  5 JTU, 50 JTU  $\pm$  10 JTU, and (100 JTU  $\pm$  20 JTU (Purchase Description, Annex A).
  - 2) pH. The measurements of pH will be within the range of 3.0 to 11.0 units for selection of water sources and checking ion exchange for column exhaustion and regeneration rinse requirements in the operation of ion exchange equipment and for determining the minimum acid requirements in removing scale from distillation equipment (MN(ED), ES, Section VI, para b(5)(b)). The accuracy of the kit shall be as follows:  $\pm$ 0.5 unit at all pH values (Purchase Description, Annex N).
  - 3) Chlorine-Residual. Chlorine residual measurements using the Modified Orthotolidine-Arsenite Test or future developmental item shall be capable of determining free and total residual chlorine in the range of 0.1 to 10 mg/l for adjustment of calcium hypochlorite dosage with field purification equipment (MN(ED), ES, Section VI, para b(5)(c)).

4) Chlorides. Chloride measurements will be within the range of 10 to 1000 mg/l for selection of proper water treatment process. Chloride determination is also required in the operation of distillation equipment to measure raw water contamination of distillate due to heat exchange or evaporator tube leakage, priming, foaming or other adverse operational characteristics (MN(ED), ES, Section VI, para b(5)(d)). The accuracy of the kit shall be as follows: 25 mg/l  $\pm$  13 mg/l, 250 mg/l  $\pm$  29 mg/l, 600 mg/l  $\pm$  55 mg/l, and 1000 mg/l  $\pm$  70 mg/l (Purchase Description, Annex B).

5) Sulfates. The sulfate measurements will be within the range of 100 to 3000 mg/l for selection of water source and treatment process to be used. Sulfate measurements also determine scaling potential of water and prescribe operating procedures for distillation equipment (MN(ED), ES, Section VI, para b(5)(e)). The accuracy of the kit shall be as follows: 250 mg/l  $\pm$  78 mg/l, 400 mg/l  $\pm$  106 mg/l and 2700 mg/l  $\pm$  502 mg/l (Purchase Description, Annex C).

6) Hardness. The hardness measurements will be within the range of 20 to 9000 mg/l as calcium carbonate ( $\text{CaCO}_3$ ) to determine the exhaustion of the softening capacity of ion exchange resins and their operating cycle duration. Hardness measurements are essential to anticipate logistical support for operation of ion exchange softening. Test shall also permit measurement of calcium hardness to determine the calcium sulphate scaling potential of brackish waters. Calcium hardness determination is also required to calculate magnesium content of water (MN(ED), ES, Section VI, para b(5)(f)). The accuracy of the kit shall be as follows: 250 mg/l  $\pm$  33 mg/l and 9000 mg/l  $\pm$  600 mg/l (Purchase Description, Annex D).

7) Chlorine Demand. The chlorine demand test procedure, with the aid of the chlorine residual test apparatus, shall be used as a guide for selection of water source and determining the amount of chlorine needed to treat a given source of water. The chlorine demand is indicative of the degree of contamination which is a valuable indicator for suspected gross area contamination (MN(ED), ES, Section VI, para b(5)(g)). The chlorine reagent shall be of the tablet form and shall be formulated so that one tablet when added to 200 ml of water shall add 5 ppm  $\pm$  0.5 ppm chlorine to the water (Purchase Description, Annex E).

8) Alkalinity. The alkalinity measurements will be within the range of 5 to 500 mg/l as a calcium carbonate ( $\text{CaCO}_3$ ) which is an indication of scaling potential in the distillation of saline waters. The amount of acid used to remove magnesium hydroxide scale, is directly proportional to the alkalinity of the feed water (MN(ED), ES, Section VI, para b(5)(h)). The accuracy of the kit shall be as follows: 120 mg/l  $\pm$  10 mg/l and 500 mg/l  $\pm$  50 mg/l (Purchase Description, Annex F).

9) Color. Color measurements will be within the range of 10 to 200 units as an aid in the selection of a water source (MN(ED), ES, Section VI, para b(5)(i)). The accuracy of the test shall be as follows: 15 units  $\pm$  5 units and 50 units  $\pm$  15 units (Purchase Description, Annex G).

10) Coagulation Tests. Equipment for performing coagulation tests to determine optimum chemical dosages in coagulation processes shall be included to aid in selection of water source and maintain efficient operation of coagulation-filtration processes (MN(ED), ES, Section VI, para b(5)(j)). The ferric chloride solution shall be contained in plastic bottles with droppers or in self-contained dropper bottles. The ferric chloride solution shall be formulated so that one drop of solution is equivalent to 10 ppm of ferric chloride when added to 200 ml of water (Purchase Description, Annex E).

11) Total Dissolved Solids. The sets shall include a conductivity meter calibrated in milligrams per liter of total dissolved solids. The meter shall be capable of determining the total dissolved solids in 1 to 50 and 50 to 5000 mg/l ranges (MN(ED), ES, Section VI, para b(5)(m)).

b. The Water Quality Analysis Set, Preventive Medicine, shall provide equipment, chemicals, and accessories to permit the operator to perform all of the tests prescribed by the Water Quality Analysis Set, Engineer (para 2.3.2a above) and the following additional tests (MN(ED), PMS, Section VI, para b(5)) (See Appendix IIB for tolerances):

- 1) Turbidity. Measurements shall be capable of detecting the presence of turbidity in the range of 5 to 500 units (MN(ED), PMS, Section VI, para b(5)(c); CTP Revision 1, Table III).
- 2) Zinc. Measurements shall be capable of detecting the presence of zinc in the range of 1 to 20 mg/l (MN(ED), PMS, Section VI, para b(5)(d)).
- 3) Fluoride. Measurements shall be capable of detecting the presence of fluoride in the range of 0.1 to 10.0 mg/l (MN(ED), PMS, Section VI, para b(5)(e)).

Find 2

- 3) Barium. Measurements shall be capable of detecting barium in the range of 0.1 to 5.0 mg/l (MN(ED), MLS, Section VI, para b(5)(c)).
- 4) Cadmium. Measurements shall be capable of detecting the presence of cadmium in the range of 0.001 to 0.100 mg/l (MN(ED), MLS, Section VI, para b(5)(d)).
- 5) Chromium ( $Cr^{+6}$ ). Measurements shall be capable of detecting the presence of chromium in the range of 0.01 to 1.0 mg/l (MN(ED), MLS, Section VI, Para b(5)(e)).
- 6) Cyanide. Measurements shall be capable of detecting cyanide in the range of 0.10 to 5.00 mg/l (MN(ED), MLS, Section VI, para b(5)(f)).
- 7) Lead. Measurements shall be capable of detecting lead in the range of 0.01 to 1.00 mg/l (MN(ED), MLS, Section VI, para b(5)(g)).
- 8) Mercury. Measurements shall be capable of detecting mercury in the range of 0.001 to 0.100 mg/l (MN(ED), MLS, Section VI, para b(5)(h)).
- 9) Ammonia Nitrogen ( $NH_3$ ). Measurements shall be capable of detecting ammonia nitrogen ( $NH_3$ ) in the range of 0.001 to 0.100 mg/l (MN(ED), MLS, Section VI, para b(5)(i)).
- 10) Selenium. Measurements shall be capable of detecting selenium in the range of 0.001 to 0.100 mg/l (MN(ED), MLS, Section VI, para b(5)(j)).
- 11) Sulfates. Measurements shall be capable of detecting sulfates in the range of 10.0 to 3000 mg/l (MN(ED), MLS, Section VI, para b(5)(k)).
- 12) Copper. Measurements shall be capable of detecting the presence of copper in the range of 0.1 to 5.0 mg/l (MN(ED), MLS, Section VI, para b(5)(l)).

#### 2.3.3 Method (Method utilized is bracketed)

[ Standard solutions of known concentrations will be made, using the individual elements and/or compounds that a specific test set is designed to detect. These solutions will be used to determine the ability of the set to detect the ingredient in the concentrations specified. ]

The following test will be conducted to determine if individual elements and/or compounds, when mixed with other elements and/or

compounds, act synergistically to interfere with the detection of the given ingredient that a test set is supposed to detect:

- a. The test set will be used to detect and identify concentrations of ingredients in a series of solutions with known quantities of mixed ingredients added to double-distilled water. These solutions will be mixed based on known interference conditions as specified by the standard methods.
- b. Three samples of water from various local sources (i.e., tap, stream, and bay water) will be analyzed in the laboratory for content and concentration. The ES will then be used to detect and identify the concentration of ingredients that have been determined to be present in the water sample.

[ The series of tests, except for those conducted to determine interferences, will be conducted both prior to and after the environmental subtest (para 2.4) to determine the ability of the ES, PMS, and MLS to withstand the environmental conditions specified. ]

Testing will be performed by laboratory personnel under laboratory conditions in a temperature- and humidity-controlled environment. Each analysis performed will be accomplished using the instructions provided for each of the test sets.

The quality of performance of the test sets (ES, PMS, and MLS) will be determined by means of instrumental and analytical chemistry techniques.

#### 2.3.4 Data Required and Analytical Plan (Data Required utilized is bracketed)

2.3.4.1 Engineer Set. The following data is required:

a. Turbidity:

- 1) Measurement range, Jackson turbidity units (JTU).
- 2) Accuracy at:
  - a) 5 JTU.
  - b) 50 JTU.
  - c) 100 JTU.

b. pH:

- 1) Measurement range, pH (units).
- 2) Accuracy at all pH values.

c. Chlorine Residual. Measurement range for determining free and total residual chlorine, in mg/l.

d. Chlorides:

- 1) Measurement range, mg/l.
- 2) Accuracy at:
  - a) 25 mg/l.
  - b) 250 mg/l.
  - c) 600 mg/l.
  - d) 1000 mg/l.

e. Sulfates:

- 1) Measurement range, mg/l.
- 2) Accuracy at:
  - a) 250 mg/l.
  - b) 400 mg/l.
  - c) 2700 mg/l.

f. Hardness as  $\text{CaCO}_3$ :

- 1) Measurement range, mg/l.
- 2) Accuracy at:
  - a) 250 mg/l.
  - b) 9000 mg/l.

g. Chlorine Demand:

- 1) Concentration of chlorine, ppm.
- 2) Concentration accuracy of chlorine reagent tablets, ppm.

h. Alkalinity as  $\text{CaCO}_3$ :

- 1) Measurement range, mg/l.

[ 2) Accuracy at:  
    a) 120 mg/l.  
    b) 500 mg/l. ]

i. Color:

1) Measurement range, color units.

2) Accuracy at:

a) 15 units.  
b) 50 units.

j. Problems. Any problems encountered with the coagulation test.

k. Range. Measurement range for determining total dissolved solids, mg/l.

2.3.4.2 Preventive Medicine Set. All the data indicated in paragraph 2.3.4.1, plus the following data, will be obtained to the nearest 0.1% of value:

a. Turbidity:

1) Measurement range, JTU.

2) Accuracy at:

a) 5.0 JTU.  
b) 500 JTU.

b. Zinc:

1) Measurement range, mg/l.

2) Accuracy at 5 mg/l.

Table 4-1  
Chloride Test Results

Sample No.	Solution 1 1200 ppm Cl <sup>-</sup>	Solution 2 1000 ppm Cl <sup>-</sup>	Solution 3 600 ppm Cl <sup>-</sup>	Solution 4 250 ppm Cl <sup>-</sup>	Solution 5 36 ppm Cl <sup>-</sup>
1	1320 *	1020	600	231	<36
2	1170	1080 -	600	231	<36
3	1200	1080 -	615	222	<36
4	1140	960	600	240	<36
5	1170	1080 -	615	231	<36
6	1170	1110 -	585	231	36
7	1200	1110 -	600	231	<36
8	1020 *	1080 -	615	222	36
9	1020 *	1080 -	660	222	36
10	1140	1080 -	600	222	<36
11	1170	1020	600	222	36
12	1200	1080 -	600	222	36
13	1170	1080 -	630	222	<36
14	1200	1080 -	585	231	36
15	1140	1080 -	600	231	36
16	1140	1110 -	600	222	36
17	1200	1080 -	540	213	36
18	1200	1110 -	615	222	36
19	1200	1110 -	600	150	36
20	1200	1110 -	615	240	<36
21	1200	1080 -	600	240	<36
22	1200	1080 -	630	222	<36
23	1170	1040	585	240	36
24	1200	1110 -	540	222	36
25	1140	1110 -	570	222	36
26	1170	1080 -	570	222	36
27	1200	1020	510	222	<36
28	1170	1080 -	585	213	36
29	1170	1080 -	600	222	36
30	1200	1080 -	600	222	<36
31	1140	1080 -	660	231	<36
32	1170	1110 -	600	213	36
33	1170	1080 -	585	231	<36
34	1170	1110 -	600	240	<36
35	--	1110 -	570	240	<36
36	--	1140 -	615	222	36
37	--	1110 -	600	222	--
38	--	1080 -	675	231	--
39	--	1080 -	675	240	--
40	--	1110 -	585	222	--
41	--	1140 -	585	231	--
42	--	1110 -	675	240	--

100/2

Table 4-1  
Chloride Test Results  
Cont.

Sample No.	Solution 1 1200 ppm Cl <sup>-</sup>	Solution 2 1000 ppm Cl <sup>-</sup>	Solution 3 600 ppm Cl <sup>-</sup>	Solution 4 250 ppm Cl <sup>-</sup>	Solution 5 36 ppm Cl <sup>-</sup>
43	—	1080	670	222	—
44	—	1110	585	222	—
45	—	1080	615	222	—
46	—	1080	600	231	—
47	—	1110	585	336	—
48	—	1080	600	231	—
49	—	1080	540	231	—
50	—	1080	600	240	—
51	—	1080	630	231	—
52	—	1110	615	231	—
53	—	1080	630	240	—
54	—	1020	630	240	—
55	—	960	615	231	—
56	—	960	540	240	—
57	—	960	600	240	—

7-16-61

Table 4-2  
Alkalinity Test Results

Sample No.	Solution 1 7500 mg CaCO <sub>3</sub> /l (0.6% NaOH)	Solution 2 500 mg CaCO <sub>3</sub> /l	Solution 3 125 mg CaCO <sub>3</sub> /l (0.01% NaOH)	Solution 4 120 mg CaCO <sub>3</sub> /l
1	6600	550	100	125
2	6600	450	75	125
3	6600	550	100	125
4	7850	550	100	75
5	7500	450	125	125
6	7150	450	75	125
7	7500	450	100	125
8	6600	500	125	100
9	7150	450	125	100
10	7150	500	125	125
11	7150	550	125	75
12	7500	500	100	125
13	7150	500	125	100
14	7150	450	125	100
15	6600	500	125	125
16	7150	550	125	100
17	7150	550	100	125
18	7150	550	125	125
19	7500	450	125	100
20	7150	450	125	100
21	7150	550	125	125
22	7150	500	125	125
23	7150	550	100	100
24	7150	550	125	100
25	7150	550	125	100
26	7500	500	125	125
27	7500	550	100	100
28	7150	500	100	100
29	7500	450	100	125
30	7500	500	100	125
31	6600	550	100	100
32	7500	450	100	125
33	—	450	125	125
34	—	450	100	125
35	—	450	125	125
36	—	400	125	125
37	—	450	125	125
38	—	450	125	100
39	—	425	100	125
40	—	450	125	125
41	—	450	100	125

Table 4-2  
Alkalinity Test Results  
Cont.

Sample No.	Solution 1 7500 mg CaCO <sub>3</sub> /l (0.6% NaOH)	Solution 2 500 mg CaCO <sub>3</sub> /l	Solution 3 125 mg CaCO <sub>3</sub> /l (0.01% NaOH)	Solution 4 120 mg CaCO <sub>3</sub> /l
42	—	450	125	100
43	—	425	125	125
44	—	500	75	75
45	—	550	100	125
46	—	550	125	100
47	—	550	125	100
48	—	500	75	125
49	—	450	100	125
50	—	500	100	125
51	—	450	125	125
52	—	550	125	100
53	—	—	—	100

Ind 3

Table 4-3  
Hardness Test Results

Sample No.	Solution 1 0 ppm CaCO <sub>3</sub>	Solution 2 20 ppm CaCO <sub>3</sub>	Solution 3 250 ppm CaCO <sub>3</sub>	Solution 4 425 ppm CaCO <sub>3</sub>
1	0	13	120	120
2	0	25	120	120
3	0	25	120	250
4	0	25	120	120
5	0	25	185	185
6	0	13	120	185
7	0	13	120	120
8	0	25	120	120
9	0	25	120	120
10	0	25	85	185
11	0	25	120	185
12	0	25	120	120
13	0	25	120	120
14	0	25	120	120
15	0	25	120	120
16	0	25	185	120
17	0	25	120	120
18	0	48	120	120
19	0	25	85	120
20	0	13	120	120
21	0	25	120	185
22	0	13	120	120
23	0	13	85	185
24	0	13	120	120
25	0	25	120	120
26	0	25	120	120
27	0	25	120	120
28	0	25	85	185
29	0	25	85	120
30	0	13	120	120
31	0	13	85	185
32	0	25	120	185
33	0	25	120	120
34	0	25	85	185
35	0	25	85	—
36	0	25	120	—
37	0	13	85	—
38	0	25	85	—
39	0	25	185	—
40	0	25	120	—
41	0	48	120	—
42	0	25	85	—

Ind 3

TECHNICAL LIBRARY  
BLDG. 305  
ABERDEEN PROVING GROUND, MD.  
STEAP-TL

Table 4-3  
Hardness Test Results  
Cont.

Sample No.	Solution 1 0 ppm CaCO <sub>3</sub>	Solution 2 20 ppm CaCO <sub>3</sub>	Solution 3 250 ppm CaCO <sub>3</sub>	Solution 4 425 ppm CaCO <sub>3</sub>
43	0	25	85	—
44	0	25	85	—
45	0	25	85	—
46	0	25	120	—
47	0	25	120	—
48	0	13	120	—
49	0	13	85	—
50	0	25	85	—
51	0	13	85	—
52	0	25	85	—
53	0	48	120	—
54	0	13	85	—
55	0	13	85	—
56	0	25	120	—
57	0	25	85	—
58	0	13	120	—
59	0	25	120	—
60	0	25	120	—

Incl 3

Table 4-4  
 Calculated Results for Chloride Test  
 Range 36-1200 ppm Cl<sup>-</sup>

Known Concentration	36ppm	250ppm	600ppm	1000ppm	1200ppm
No. of Measurements	36	57	57	57	34
Average Concentration	236	299.1	600.4	1077.7	1170.9
Standard Deviation	—	19.45	26.50	41.36	50.89
Deviation (Avg-Known Conc)	<0	49.1	0.4	77.7	-29.1
95% Conf. Interval on Mean					
Lower Limit	—	293.9	593.4	1066.8	1153.1
Upper Limit	—	304.2	607.5	1088.7	1188.6
Accuracy Requirement Interval	—	250±29	600±55	1000±70	—
Lower Limit	—	221	545	930	—
Upper Limit	—	279	655	1070	—
95% Tolerance Interval (p=0.90)					
Lower Limit	—	260.8	548.3	996.3	1064.0
Upper Limit	—	337.4	652.6	1159.2	1277.8

Ind 3

Table 4-5  
 Calculated Results for Alkalinity Test  
 Range 0.01-0.6% NaOH

Known Concentration	120 mg CaCO <sub>3</sub> /l	125 mg CaCO <sub>3</sub> /l (0.01% NaOH)	500 mg CaCO <sub>3</sub> /l	7500 mg CaCO <sub>3</sub> /l (0.6% NaOH)
No. of Measurements	53	52	52	32
Average Concentration	113.2	112.0	492.3	7167.2
Standard Deviation	15.19	16.03	46.58	331.08
Deviation (Avg-Known Conc)	-6.8	-13.0	-7.7	-332.8
95% Conf. Interval on Mean				
Lower Limit	109.0	107.6	479.3	7047.8
Upper Limit	117.4	116.5	505.3	7286.6
Accuracy Requirement Interval	120±10	—	500±50	—
Lower Limit	110	—	450	—
Upper Limit	130	—	550	—
95% Tolerance Interval (p=0.90)				
Lower Limit	83.1	79.8	398.8	6465.3
Upper Limit	143.4	144.2	585.8	7809.1

Incl 3

Table 4-6  
 Calculated Results for Hardness Test  
 Range 0-425 ppm CaCO<sub>3</sub>

Known Concentration	0 ppm	20 ppm	250 ppm	425 ppm
No. of Measurements	60	60	60	34
Average Concentration	0	23.0	111.0	142.9
Standard Deviation	0	7.85	23.84	35.36
Deviation (Avg-Known Conc)	0	3.0	-139.0	-282.1
95% Conf. Interval on Mean				
Lower Limit		20.9	104.8	130.6
Upper Limit		25.0	117.2	155.3
Accuracy Requirement Interval	—	—	250±33	—
Lower Limit	—	—	217	—
Upper Limit	—	—	283	—
95% Tolerance Interval (p=0.90)				
Lower Limit		7.6	64.3	68.7
Upper Limit		38.3	157.7	217.2

Incl 3

Figure I  
Chloride Deviation

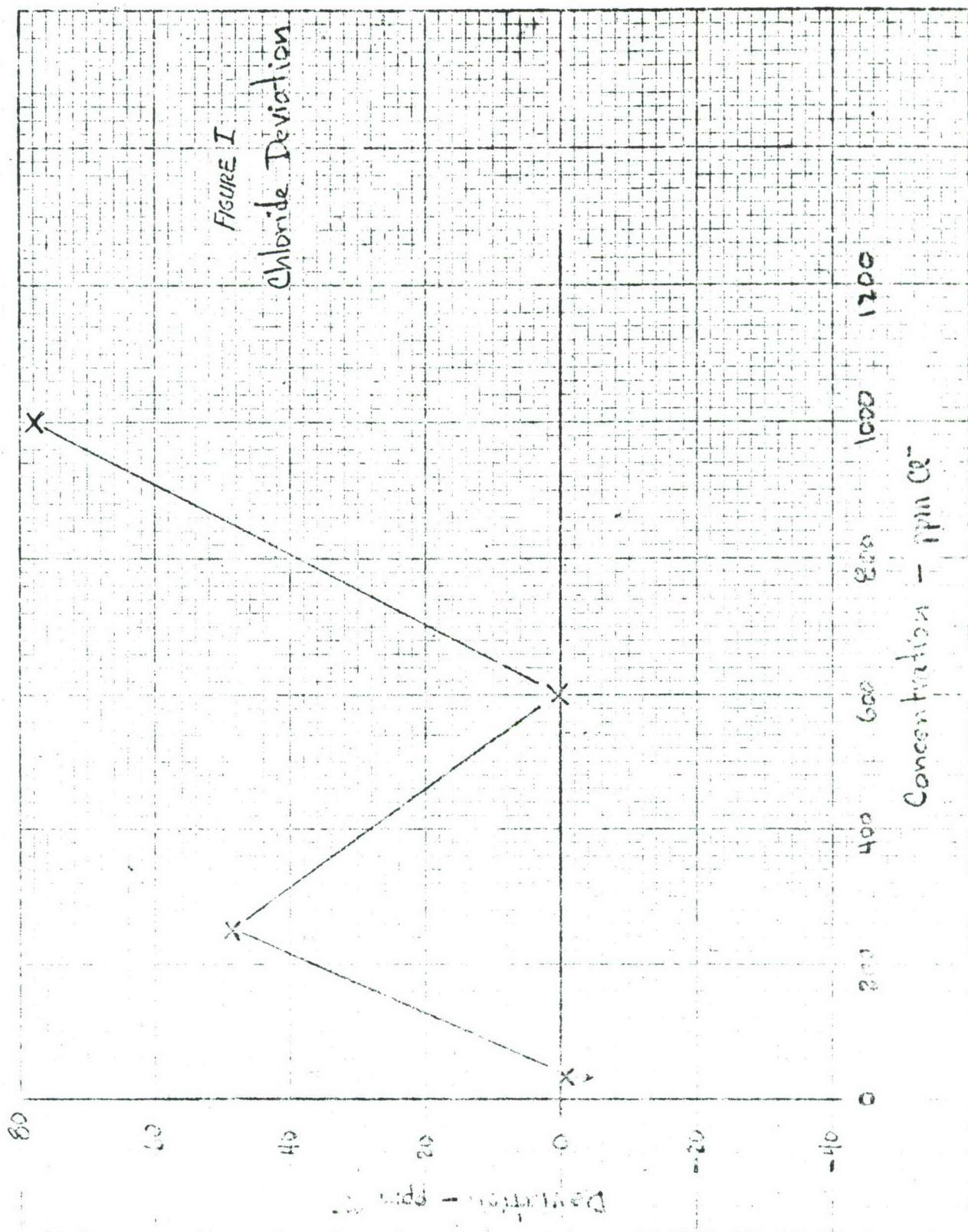


FIGURE II  
Alkalinity Deviation

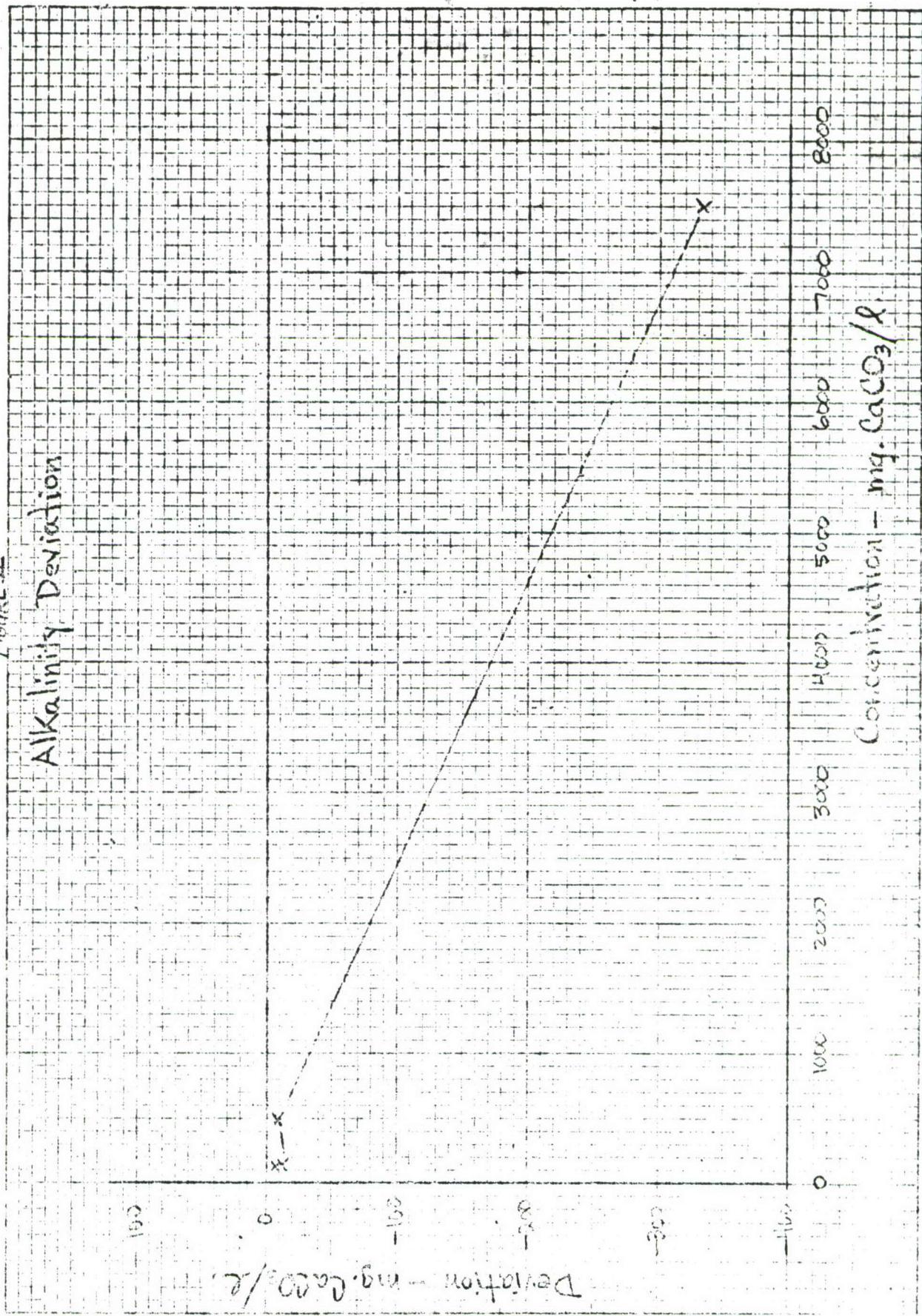
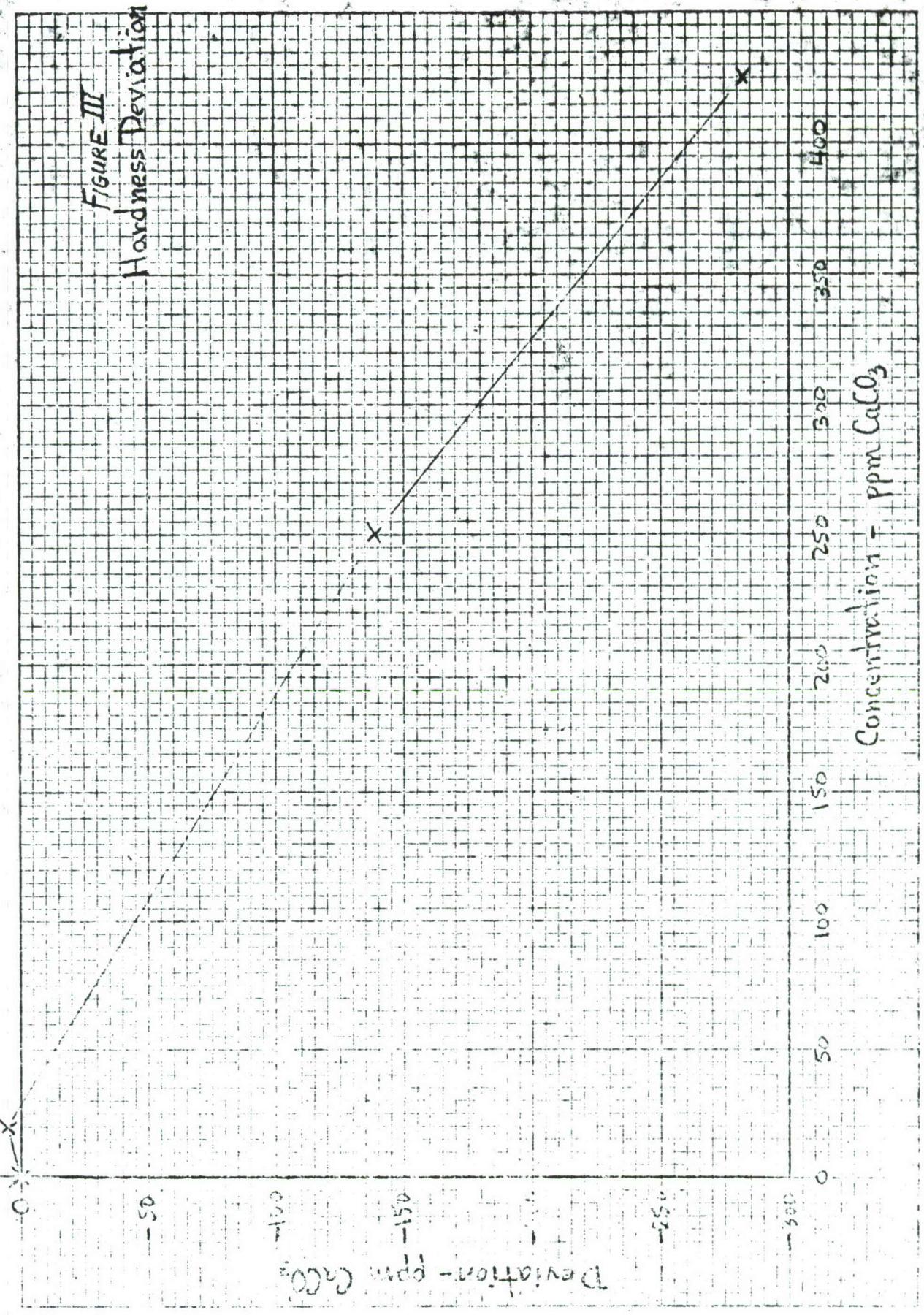


FIGURE III  
Hardness Deviation



APPENDIX B

IMPROVED TEST FOR SULFATE IN WATER LWL TASK 01-B-74

## 1. INTRODUCTION

The present test for sulfate uses a barium chloride - gelatin coating on a glass microscope slide. This proved unsatisfactory in that the gelatin coating dried and cracked with time. The glass slide was fragile.

While these two drawbacks can undoubtedly be overcome by using the coating, suitably tanned, on a transparent plastic backing, similar to photographic film, a paper strip test method was more desirable.

## 2. CONCLUSIONS

A. A paper strip impregnated with barium chloranilate provides a useful method for the detection and measurement of sulfate ion concentrations in water when the water is allowed to rise by capillary attraction up the paper. The presence of sulfate ion is evinced by a decolorization of the brown barium salt and the length of strip decolorized is a measure of the sulfate ion concentration.

B. The test strips are best made by first soaking in barium chloride solution, then in acetone and after drying, by a final soak in a solution of chloranilic acid. A wick section containing chloranilic acid only is left on the strips for immersion in the test water.

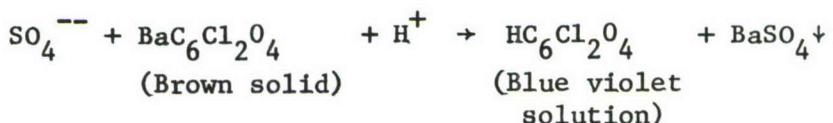
C. The presence of chloranilic acid in the wick section of the paper is necessary to minimize by common ion effect the loss of barium chloranilate from the paper in blank runs.

D. The test papers are not rigid enough when wet to stand in the water without collapse. Therefore, they are suspended in the water during the test. Alternatively, the papers can be backed with rigid plastic when suitable equipment is available.

E. The test system can be utilized to detect and determine chloride ions by substituting silver chloranilate for barium chlorinate.

### 3. THEORETICAL

In 1957, Bertolacini and Barney<sup>1</sup> described a new method for the colorimetric determination of sulfate based on the reaction of solid barium chloranilate\* with sulfate ion at pH 4 in aqueous ethyl alcohol solution to liberate the highly colored acid chloranilate ion. The method depends for its success on the insolubility of barium sulfate and the only slight solubility of barium chloranilate.



The principle of this method has potential for wide applicability. Thus, Coutinho and Almeida<sup>2</sup> who made the original discovery, used the method for the determination of chloride ion. In this case, the silver salt of chloranilic acid was used.

In the reaction



where  $Y^-$  is the anion to be determined and  $A^-$  is a colored anion of an organic acid,  $MY^-$  must be so much less soluble than  $MA^-$  that the reaction is quantitative.  $MA^-$  must be only sparingly soluble so that blanks will not be too high.

Bertolacini and Barney carried out the reaction for sulfate ion in 50% aqueous ethanol so as to depress further the solubility of barium chloranilate and hence increase the sensitivity of the method.

In our work on the development of a test strip, it is impractical to use aqueous ethanol, and we did encounter difficulties due to the significant solubility of barium chloranilate in water. This was noticed both

\* Chloranilic acid is 2,5- dihydroxy; 3,6- dichloro benzoquinone.

when strips were washed to remove barium chloride and in running the strips in distilled water for blank calibration.

These difficulties were both overcome in a simple manner by the method of strip preparation.

## 4. EXPERIMENTAL

### 4.1 PREPARATION OF BARIUM CHLORANILATE

The method used by Bertolacini loc. cit involving the mixing of aqueous solutions of barium chloride (5%) and chloranilic acid (0.1%) is tedious so the following procedure was used.

1g of chloranilic acid was dissolved in 40 mls of boiling acetic acid and mixed with a hot solution of 3g of barium acetate in 20 mls of acetic acid. The brown precipitate was centrifuged down, stirred with aqueous acetic acid (50:50) and vacuum filtered. The product was washed with distilled water, acetone and dried to give a brown powder.

The powder when stirred with water containing sulfate ions gave a blue violet solution.

### 4.2 EXPERIMENTS WITH FILTER PAPER STRIPS

A roll of Whatman 3MM chromatography paper was used throughout for the preparation of test strips which were cut 1-cm wide in lengths at right angles to the grain of the paper. (This is along the length of the roll.)

A line of brown salt was applied with a spatula to a paper and the paper dipped in distilled water so that the water rose through the salt. No pink color appeared.

Then, a second paper similarly treated was dipped in  $\text{SO}_4^{--}$  containing water. As the water rose through the brown line, a violet color developed and travelled in a diffuse manner with the water front.

It was noted that eventually the brown line disappeared, i.e., it had all been turned into  $\text{Ba SO}_4$  and chloranilic acid the latter being washed up in the paper.

The brown powder was then spread lightly over the whole of the strip

except for the wick. On running sulfate through this strip, one could clearly see a spreading area of decolorization as the water rose through the coated paper. Because of the unevenness of the coating, the result was unsatisfactory. Clearly, however, this is the way to run the test, that is by observing the removal of barium chloranilate rather than looking for the colored chloranilate ion.

#### 4.3 EXPERIMENTS WITH PAPERS IMPREGNATED WITH BARIUM CHLORANILATE

0.5g of chloranilic acid was stirred to solution with 500 mls of distilled water and the solution filtered through glass wool to remove traces of solid.

Paper was then soaked in the violet solution, air dried, and then dipped into dilute aqueous barium chloride. The paper immediately turned brown. It was washed with distilled water and dried. Strips of this paper worked very well when dipped into solutions containing sulfate ion in various concentrations. For a given height run by the solvent-front, the height of the decolorized portion varied as the sulfate concentration.

For measurement of the height of strip decolorized, one needs a starting line. Therefore, strips were made where a small length of the strip was not immersed in the dye. After drying and immersion in barium chloride, a line was drawn at the edge of the brown. 4% barium chloride was used. This line then served as the point from which measurements were made to relate  $\text{SO}_4^{--}$  concentration to height of brown decolorized. The strips were immersed to a depth such that the line remained above the liquid.

At this point, it was also determined that treatment of the dye impregnated paper with silver nitrate solution gave a reddish brown deposit in the papers which would detect chloride ion.

#### 4.4 METHOD FOR COATING THE PAPER

Having established the basis for the test, it remained to standardize the procedure for making the strips so as to give a reliable test strip

for the range required and one that could be duplicated.

After a good deal of experimentation in which various snags were encountered, the following procedure was adopted as the most dependable and involved the following critical factors:

- A. The coating should be uniform.
- B. The strips should be free of excess barium chloride.
- C. Washing of the coated strips should be avoided since the barium chloranilate dissolves out.
- D. Blank readings should be reduced as much as possible.

#### 4.5 PROCEDURE

- A. Cut 10cm squares of Whatman 3MM paper.
- B. Make up solutions in distilled water of 0.1% chloranilic and 0.4% barium chloride (4g of  $BaCl_2 \cdot 2H_2O$  liter).
- C. Place the barium chloride in a flat bottomed tank big enough to accommodate a 10cm paper square and deep enough for a 6cm height of liquid.
- D. Lower paper square into the barium chloride until the bottom edge touches the base of the tank and remove the square. The square should be oriented so that the grain is parallel to the liquid surface.
- E. After removal from the barium chloride, immediately lower the whole square into a tank containing at least 1 liter of acetone and then put the square into a hot air oven at about  $100^{\circ}C$ .

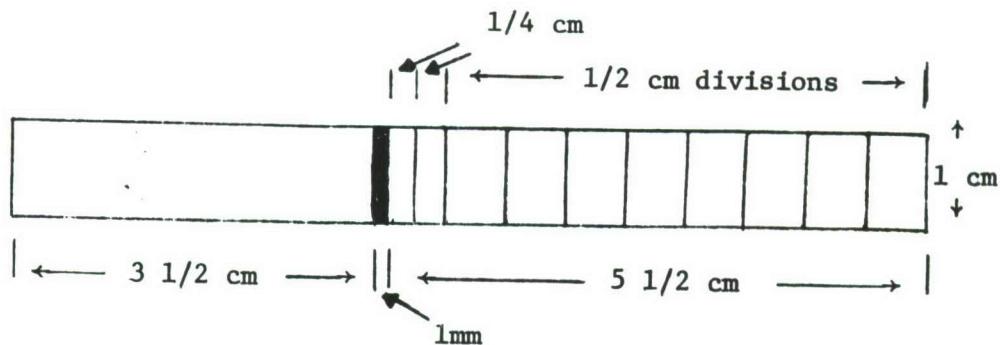
The reason for this acetone bath is that if the papers are dried when wet with aqueous solutions, the liquid tends to diffuse into the dry part and leaves a more dilute deposit of solute there.

- F. When dry slide the square under the surface of the 0.1% chloranilic acid contained in a shallow enamel tray. Rock the liquid back and forth (as in photography) for 1 minute, then hand the paper up by the uncoated part to air dry.

The result should be a square, pale blue-violet at the top and brown below with a good sharp straight line of demarcation between the two colors.

The upper blue violet part will become the wick and the chloranilic acid in it will help to depress the elution of barium chloranilate from the test strip in blank runs and runs of low  $SO_4^{2-}$  concentration. (Law of mass action.)

G. When dry, the square is measured and pencil lined according to the following dimensions:



The  $1$  cm heavy line is to blank out the small result with distilled water. The first two  $1/4$  cm divisions are for  $50$  and  $100$  ppm  $\text{SO}_4^-$ .

H. Since it is difficult to run the strips by standing them in a layer of water (they tend to collapse) and because of errors that might crop up by evaporation from a strip in an open container, a closed system involving suspension of the strips was devised.

This consists of a  $2$  oz. screw cap dropping bottle with an alligator clip in the rubber bulb (instead of the dropper). Water under test is poured into the bottle in an amount not to exceed the level marked on the bottle. The test strip is then clipped so that the clip reaches the highest graduation and then inserted in the bottle and the cap screwed down.

When the water reaches the top of the strip (about  $6$  min.), the strip is read by reference to a graph showing length of white portion versus ppm  $\text{SO}_4^-$ .

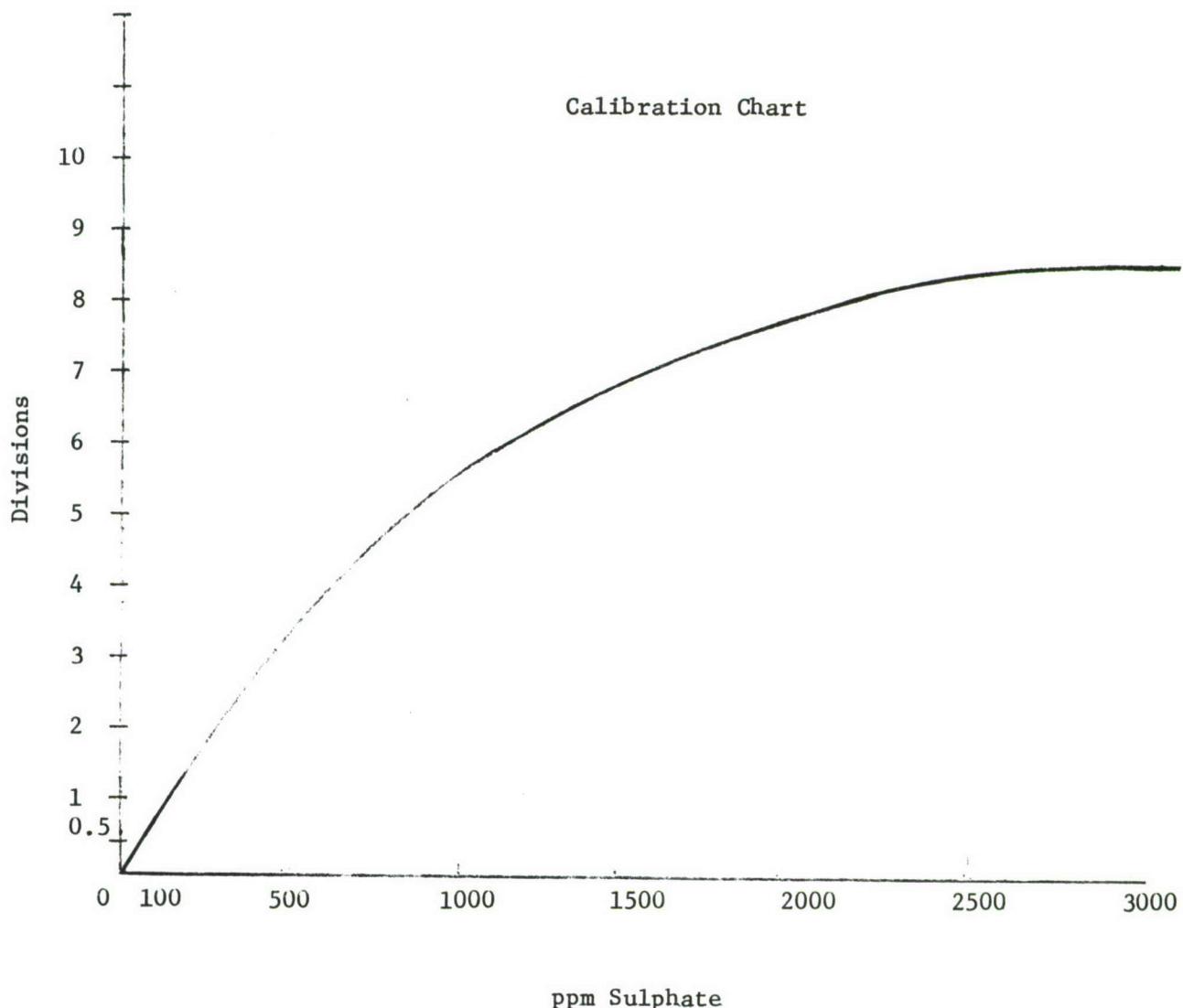
#### 4.6 CALIBRATION

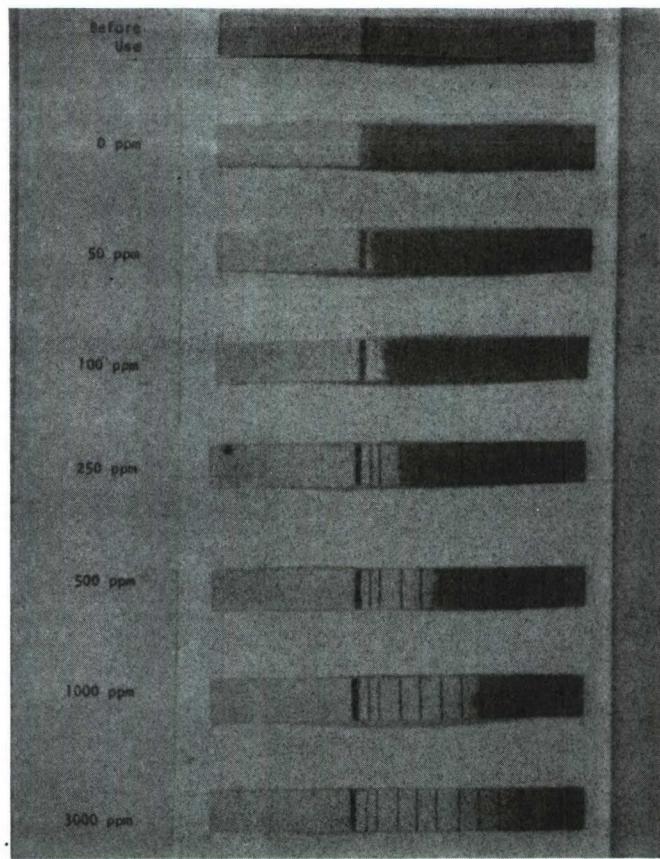
The highest sulfate ion concentration to be detected is  $3000$  ppm or  $3$  g per liter. This is contained in  $4.439$  g of anhydrous sodium sulfate which was weighed out and made up to  $1$  liter with distilled water.

Suitable dilutions gave solutions containing  $1000$ ,  $500$ ,  $250$ ,  $100$

and 50 ppm sulfate ion.

A sample paper strip from each batch was first tested in distilled water to ensure that the blank reading was within the 1mm region. Batches that passed this test were retained and a set run in each of the above solutions. The length of barium chloranilate decolorized was then measured and plotted against sulfate concentration. From this calibration curve, an example of which is shown below, the sulfate concentration of an unknown can be estimated.





**Photograph of Test Strips**

## SAMPLE INSTRUCTION SHEET

Clip test strip so that clip reaches the top graduation of colored part of the strip.

Put test liquid in bottle up to, but not over, level marked on bottle.

Insert paper into the bottle and screw down cap.

When liquid has risen to the top of the strip (about 6 min.), remove and determine  $\text{SO}_4^{2-}$  concentration by reference to the calibration chart.

## 5. REFERENCES

1. R.I. Bertolacini and J.E. Barney, Anal. Chem., 29(2) 281 (1957).
2. A.B. Coutinho and M.D. Almeida, Anais, assoc. quím. Brasil, 10 83 (1951).

## APPENDIX

### 1. Reagents and Supplies

Chloranilic acid. Pfaltz & Bauer, Flushing, NY.

Barium Chloride.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , Mallinckrodt.

Chromatography paper. Whatman 3MM, 18" width and 300 foot roll.

Sodium Sulphate. "Baker Analyzed" Reagent anhydrous Powder.

### 2. Sample Instruction Sheet

Clip test strip so that clip reaches the top graduation of colored part of the strip.

Put test liquid in bottle up to but not over level marked on bottle.

Insert paper into the bottle and screw down cap.

When liquid has risen to the top of the strip (about 6 min.), remove and determine  $\text{SO}_4^{--}$  concentration by reference to the calibration chart.

DISTRIBUTION LIST

Copies

Commander US Army Materiel Command ATTN: AMCDL 5001 Eisenhower Avenue Alexandria, VA 22333	1
Commander US Army Materiel Command ATTN: AMCRD 5001 Eisenhower Avenue Alexandria, VA 22333	3
Commander US Army Materiel Command ATTN: AMCRD-P 5001 Eisenhower Avenue Alexandria, VA 22333	1
Director of Defense, Research & Engineering Department of Defense WASH DC 20301	1
Director Defense Advanced Research Projects Agency WASH DC 20301	3
HQDA (DARD-DDC) WASH DC 20310	4
HQDA (DARD-ARZ-C) WASH DC 20310	1
HQDA (DAFD-ZB) WASH DC 20310	1
HQDA (DAMO-PLW) WASH DC 20310	1
Commander US Army Training & Doctrine Command ATTN: ATCD Fort Monroe, VA 23651	1

1  
Commander  
US Army Combined Arms Combat Developments Activity  
Fort Leavenworth, KS 66027

1  
Commander  
US Army Logistics Center  
Fort Lee, VA 23801

1  
TRADOC Liaison Office  
HQs USATECOM  
Aberdeen Proving Ground, MD 21005

1  
Commander  
US Army Test and Evaluation Command  
Aberdeen Proving Ground, MD 21005

1  
Commander  
US Army John F. Kennedy Center for Military Assistance  
Fort Bragg, NC 28307

1  
Commander-In-Chief  
US Army Pacific  
ATTN: GPOP-FD  
APO San Francisco 96558

1  
Commander  
Eighth US Army  
ATTN: EAGO-P  
APO San Francisco 96301

1  
Commander  
Eighth US Army  
ATTN: EAGO-FD  
APO San Francisco 96301

4  
Commander-In-Chief  
US Army Europe  
ATTN: AEAGC-ND  
APO New York 09403

1  
Commander  
US Army Alaska  
ATTN: ARACD  
APO Seattle 98749

Commander MASSTER ATTN: Combat Service Support & Special Programs Directorate Fort Hood, TX 76544	1
Commander US MAC-T & JUSMAC-T ATTN: MACTRD APO San Francisco 96346	2
Senior Standardization Representative US Army Standardization Group, Australia c/o American Embassy APO San Francisco 96404	1
Senior Standardization Representative US Army Standardization Group, UK Box 65 FPO New York 09510	1
Senior Standardization Representative US Army Standardization Group, Canada Canadian Forces Headquarters Ottawa, Canada K1A0K2	1
Director Air University Library ATTN: AUL3T-64-572 Maxwell Air Force Base, AL 36112	1
Battelle Memorial Institute Tactical Technical Center Columbus Laboratories 505 King Avenue Columbus, OH 43201	1
Defense Documentation Center (ASTIA) Cameron Station Alexandria, VA 22314	12
Commander Aberdeen Proving Ground ATTN: STEAP-TL Aberdeen Proving Ground, MD 21005	2
Commander US Army Edgewood Arsenal ATTN: SMEA-TS-L Aberdeen Proving Ground, MD 21010	1

US Marine Corps Liaison Officer  
Aberdeen Proving Ground, MD 21005

Director  
Night Vision Laboratory  
US Army Electronics Command  
ATTN: AMSEL-NV-D (Mr. Goldberg)  
Fort Belvoir, VA 22060

Commander  
US Air Force Special Communications Center (USAFSS)  
ATTN: SUR  
San Antonio, TX 78243

Commander  
US Army Armament Command  
ATTN: AMSAR-ASF  
Rock Island, IL 61201

Commander  
US Army Troop Support Command  
ATTN: AMSTS-MF (Mr. Benn)  
St. Louis, MO 63166

Commander  
US Army Mobility Equipment Research & Development Center 2  
ATTN: STSFB-MS (Mr. R. Schmitt)  
Fort Belvoir, VA 22060